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Comparison of the Catalytic Behaviors of Single Cubane $MoFe_3S_4$ and Fe_4S_4 Clusters toward the Multi-electron Reduction of $n\text{-}C_5H_{11}N_3$

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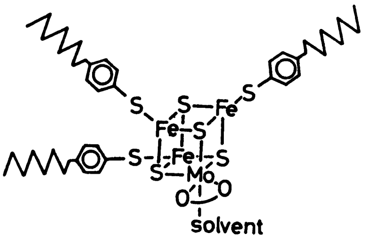
The reduction of $n\text{-}C_5H_{11}N_3$ by $Na_2S_2O_4$ was investigated in an aqueous Triton X-100 micellar solution containing methylviologen and $[MoFe_3S_4(S\text{-}p\text{-}n\text{-}C_6H_4C_8H_{17})_3(O_2C_6Cl_4)(Me_2CO)]^{2-}$ (**1**) or $[Fe_4S_4(S\text{-}p\text{-}n\text{-}C_6H_4C_8H_{17})_4]^{2-}$ (**2**). **1** catalyzes the reduction of $n\text{-}C_5H_{11}N_3$ not only with two electrons but also with six and eight electrons to afford $n\text{-}C_5H_{11}NH_2$, N_2, N_2H_4, and NH_3, while **2** catalyzes only two electron reduction of $n\text{-}C_5H_{11}N_3$.

The molybdenum-iron cofactor (MoFe-co) considered as an active center in nitrogenase (N_2ase) may involve a molybdenum-iron-sulfur cluster. The molybdenum atom in the MoFe-co is believed as a binding site to the N_2ase substrates, though no direct evidence that can eliminate the possibility of the iron atom as the active site has been provided so far. The comparison of the catalytic activities between molybdenum and iron atoms toward multi-electron reductions of N_2ase or pseudo-N_2ase substrates may, therefore, be very important in connection with the fact that the reduction of dinitrogen by N_2ase takes place with eight electrons to afford two moles of ammonia and one mole of dihydrogen. This letter reports the reduction of $n\text{-}C_5H_{11}N_3$ catalyzed by $[MoFe_3S_4(S\text{-}p\text{-}n\text{-}C_6H_4C_8H_{17})_3(O_2C_6Cl_4)L]^{2-}$ (**1**) (L = Me_2CO, DMF) and $[Fe_4S_4(S\text{-}p\text{-}n\text{-}C_6H_4C_8H_{17})_4]^{2-}$ 1) (**2**) solubilized in aqueous Triton X-100 micellar solutions containing $Na_2S_2O_4$ and methylviologen dibromide ($MVBr_2$).



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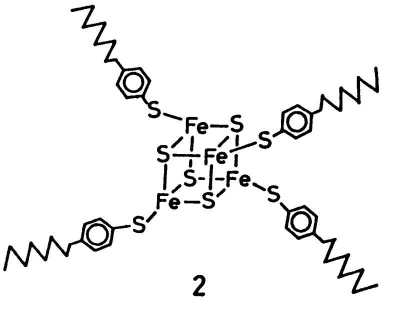

2

The cyclic voltammogram of a double $MoFe_3S_4$ cubane cluster, $(Et_4N)_4[Mo_2Fe_6S_8(S\text{-}p\text{-}n\text{-}C_6H_4C_8H_{17})_6(O_2C_6Cl_4)_2]$ 2) (**3**) in DMF exhibits a pair of cathodic and anodic waves at -1.17 and -1.10 V *vs.* SCE, respectively (curve a in Fig. 1), which

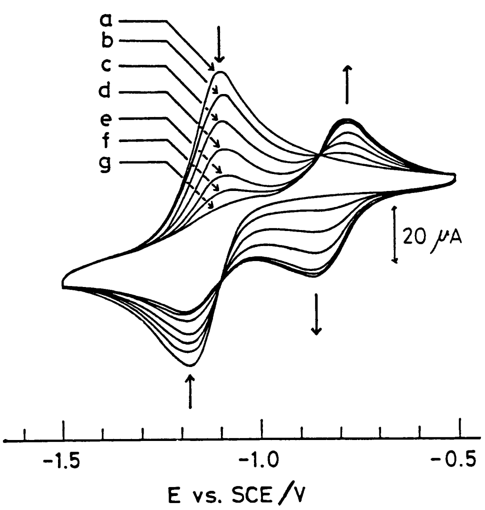

Fig. 1. Cyclic voltammograms of $[Mo_2Fe_6S_8(S\text{-}p\text{-}n\text{-}C_6H_4C_8H_{17})_6\text{-}(O_2C_6Cl_4)_2]^{4-}$ (3.3 x 10^{-3} mol dm^{-3}) in the presence of various amounts of *n*-$C_5H_{11}N_3$; 0 (a), 0.2 (b), 0.4 (c), 0.6 (d), 1.0 (e), 1.6 (f), and 3.4 x 10^{-3} mol dm^{-3} (g) in anhydrous DMF.

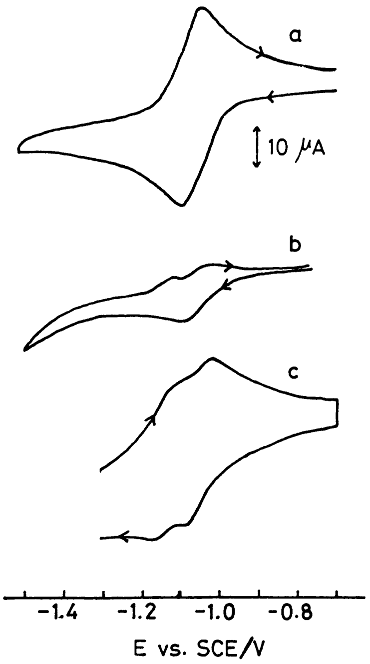

Fig. 2. Cyclic voltammograms of **2** (2.0 x 10^{-4} mol dm^{-3}) in the absence (a) and the presence (b) of *n*-$C_5H_{11}N_3$ (3.6 x 10^{-3} mol dm^{-3}), and after applying -1.30 V *vs*. SCE to a glassy carbon electrode for 3 min in the presence of *n*-$C_5H_{11}N_3$ (c) in DMF; sweep rates 100 mV s^{-1} for (a) and (c), 10 mV s^{-1} for (b).

are close to the (2-/3-) redox couple of $[MoFe_3S_4(SPh)_3(O_2C_6Cl_4)(DMF)]^{2-}$ formed by solvent induced bridging bond cleavage of an anlogous double cubane cluster $[Mo_2Fe_6S_8(SPh)_6(O_2C_6Cl_4)_2]^{4-}$ in DMF,$^{3)}$ suggesting that **3** is also dissociated into two single cubane cluster **1** (L = DMF). The solvent molecule coordinated to the molybdenum atom of $[MoFe_3S_4(SR)_3\text{-}(O_2C_6Cl_4)L]^{2-}$ (R = alkyl, aryl; L = Me_2CO, MeCN, DMF) is substituted easily by N_3^-, N_2H_4, CN^-, and RNC.$^{3)}$ In harmony with this, the addition of *n*-$C_5H_{11}N_3$ to the DMF solution of **1** results in the appearance of a new cathodic and anodic waves at -0.87 and -0.76 V, respectively; the peak currents of these waves increase with increasing the amount of *n*-$C_5H_{11}N_3$, while those of the original redox couple of **1** are weakened (curves b - g in Fig. 1). Thus, the $E_{1/2}$ value $((E_{pc} + E_{pa})/2)$ of the *n*-$C_5H_{11}N_3$ adduct formed in the substitution reaction by *n*-$C_5H_{11}N_3$ for DMF of **1** is shifted anodically by 300 mV compared with that of the DMF adduct, suggesting a decrease of an electron density in the $MoFe_3S_4$ core upon the coordination of *n*-$C_5H_{11}N_3$ to the molybdenum atom.

On the other hand, the cyclic voltammogram of the *n*-Bu_4N salt of **2** (E_{pc} = -1.08 and E_{pa} = -1.02 V *vs*. SCE) in DMF (Fig. 2a) has not been changed at all even after the addition of about 20 molar excess *n*-$C_5H_{11}N_3$ to the solution at the sweep rate 100 mV s^{-1}. When the sweep rate is decreased to 10 mV s^{-1} in the presence of excess *n*-$C_5H_{11}N_3$, however, a new anodic wave appears at -1.12 V *vs*. SCE as a shoulder (Fig. 2b). Moreover, when all the cluster 2 existing on the electrode was reduced to 3- state in the presence of excess n-$C_5H_{11}N_3$ by applying -1.30 V to the solution for 3 min, followed by the potential sweep between -1.30 and -0.70 V at 100 mV s^{-1}, a new redox couple appears at E_{pc} = -1.18 and E_{pa} = -1.12 V as shoulders (Fig. 2c). This results suggests that the 3- state of 2 slowly reacts with n-$C_5H_{11}N_3$ to form an adduct.

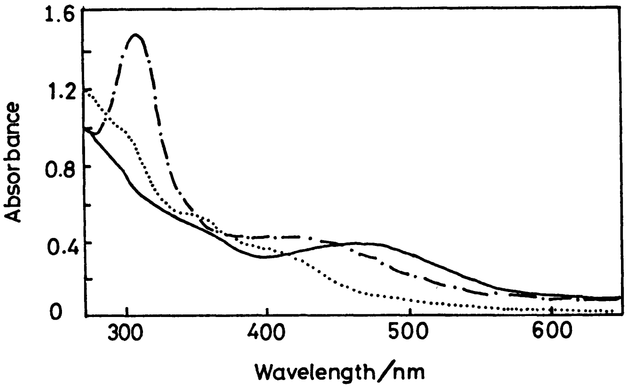

Fig. 3. The electronic absorption spectra of $[Fe_4S_4(SPh)_4]^{2-}$ (5.0×10^{-4} mol dm^{-3}) (———), and $[Fe_4S_4(SPh)_4]^{3-}$ in the absence (-----) and in the presence of n-$C_5H_{11}N_3$ (-—·—) (5.0×10^{-3} mol dm^{-3}) in DMF.

The assumption that the reduced species of 2 can interact with n-$C_5H_{11}N_3$ in solution is supported from the electronic absorption spectra of the analogous reduced cluster with the phenylthiolate ligand $[Fe_4S_4(SPh)_4]^{3-}$ in the presence and the absence of n-$C_5H_{11}N_3$; the reduced cluster in the presence of n-$C_5H_{11}N_3$ in DMF exhibits an absorption band centered at 306 nm assignable to the PhS^- anion (a dotted broken line in Fig. 3), which does not appear in the spectrum of the same species in the absence of n-$C_5H_{11}N_3$ (a dotted line in Fig. 3), whereas the spectrum of the oxidized species $[Fe_4S_4(SPh)_4]^{2-}$ (a solid line in Fig. 3) has not been changed at all even in the presence of a large excess of n-$C_5H_{11}N_3$. Moreover, the reoxidation of the reduced species $[Fe_4S_4(SPh)_4]^{3-}$ in DMF containing n-$C_5H_{11}N_3$ at -0.60 V vs. SCE for 1 h almost recovered the spectrum of the oxidized species (a solid line in Fig. 3). Such a ligand substitution reaction has been reported for the reduced species of a triply PhS^- bridged double cubane cluster $[Mo_2Fe_6S_8(SPh)_9]^{3-}$, which afforded the 1:1 adduct with MeN_3 with liberating a terminal PhS^- ligand in DMF.[4] Thus the $E_{1/2}$ value of the (2-/3-) redox couple of 2 is shifted cathodically about by 100 mV upon substitution of a thiolate ligand by n-$C_5H_{11}N_3$, suggesting an increase of the electron density of the Fe_4S_4 core upon coordination of n-$C_5H_{11}N_3$ to the iron atom.

When an Me_2CO solution of 1 or 2 was added to a stirred aqueous Triton X-100 micellar solution containing n-$C_5H_{11}N_3$ and $Na_2S_2O_4$, the reduction of n-$C_5H_{11}N_3$ took place to produce an equal amount of n-$C_5H_{11}NH_2$ and N_2 (Eq. 1) (entries 1 and 2 in Table 1). The rates of the reduction catalyzed by 1 and 2 in the presence of methylviologen dibromide ($MVBr_2$) in the reaction mixture were increased by about 20 and 50 times faster than those in the absence of $MVBr_2$, respectively. In addition, the reduction catalyzed by 1 afforded considerable amounts of N_2H_4 (Eq. 2) and NH_3 (Eq. 3) as well as N_2 and n-$C_5H_{11}NH_2$ (entry 3 in Table 1).[5] A decrease in the rate of reduction when DMF was used in place of Me_2CO as a solvent for solubilization of 1 into a micelle (entry 4 in Table 1) may be resulted from a strong coordination ability of DMF to the molybdenum atom of the $MoFe_3S_4$ core compared with that of Me_2CO. On the other hand, the reduction of n-$C_5H_{11}N_3$

Table 1. Reduction of n-$C_5H_{11}N_3$ (2.0×10^{-2} mol dm^{-3}) in aqueous Triton X-100 micellar solutions (pH 6.0) containing **1** and **2** (2.0×10^{-4} mol dm^{-3}) and $Na_2S_2O_4$ (8.0×10^{-2} mol dm^{-3}) in the absence and the presence of $MVBr_2$ at 30 °C for 1 h

Entry	Cluster	Solvent for Solubilization	MV^{2+} mol dm^{-3}	Product mol/Cluster mol			
				N_2	n-$C_5H_{11}NH_2$	N_2H_4	NH_3
1	**1**	$(CH_3)_2CO$	0	5.4	5.6	0	0
2	**2**	$(CH_3)_2CO$	0	1.1	1.4	0	0
3	**1**	$(CH_3)_2CO$	2.0×10^{-4}	90.1	75.0	0.5	20.3
4	**1**	DMF	2.0×10^{-4}	41.8	50.5	0.5	12.4
5	**2**	$(CH_3)_2CO$	2.0×10^{-4}	16.8	16.1	0	0

$$C_5H_{11}N_3 + 2e^- + 2H^+ \longrightarrow C_5H_{11}NH_2 + N_2 \tag{1}$$

$$C_5H_{11}N_3 + 6e^- + 6H^+ \longrightarrow C_5H_{11}NH_2 + N_2H_4 \tag{2}$$

$$C_5H_{11}N_3 + 8e^- + 8H^+ \longrightarrow C_5H_{11}NH_2 + 2NH_3 \tag{3}$$

catalyzed by **2** produced only n-$C_5H_{11}NH_2$ and N_2 even in the presence of MV^{2+} (entry 5 in Table 1).

Thus, **1** is superior to **2** as the catalyst of the N_2ase model reactions since neither six- nor eight-electron reduction of n-$C_5H_{11}N_3$ takes place on the iron atom under the present experimental conditions. A striking difference between **1** and 2 toward the reduction of n-$C_5H_{11}N_3$ may be associated with the fact that n-$C_5H_{11}N_3$ acts as an electron acceptor and donor to the molybdenum atom of the $MoFe_3S_4$ core and the iron atom of the Fe_4S_4 core, respectively. The present study is the first experimental support for the view that molybdenum of the MoFe-co may be the active site of N_2ase reactions.

References

1) K. Tanaka, M. Masanaga, and T. Tanaka, J. Am. Chem. Soc., 108, 5448 (1986); K. Tanaka, M. Moriya, and T. Tanaka, Inorg. Chem., 25, 835 (1986).

2) The cluster was prepared according to the procedure described in Ref. 3 and the analytical values were in good agreement with the calculated ones.

3) R. E. Palermo, R. Singh, J. K. Bashkin, and R. H. Holm, J. Am. Chem. Soc., 106, 2600 (1984).

4) S. Kuwabata, K. Tanaka, and T. Tanaka, Inorg. Chem., 25, 1691 (1986).

5) The disagreement between the amount of n-$C_5H_{11}NH_2$ and the total amounts of N_2, N_2H_4, and NH_3 formed in the reduction catalyzed by **1** in the presence of MV^{2+} (entry 3 in Table 1) results from the reaction of n-$C_5H_{11}NH_2$ with Me_2CO.

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